

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

JP 10-116631

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery using the electrolytic solution excellent in especially charge-and-discharge cycle nature, and a big negative-electrode material of service capacity about the high capacity nonaqueous electrolyte rechargeable battery excellent in the charge-and-discharge cycle property.

[0002]

[Description of the Prior Art] What used the trifluoromethane sulfonic-acid lithium for the mixed solvent which it is known that composition of nonaqueous electrolyte will influence greatly the charge-and-discharge cycle stability of nonaqueous electrolyte rechargeable batteries, such as a rechargeable lithium-ion battery, conventionally, for example, consists of the annular carbonate, the chain-like carbonate, and the ether of the amount range of specification in JP,8-64240,A as lithium salt is proposed.

[0003] Moreover, in JP,8-130036,A, using mixed solvents, such as ethylene carbonate and a chain-like carbonate, for a negative electrode at nonaqueous electrolyte using the multiple oxide of the metal of high service capacity is proposed.

[0004] Although the improvement effect of the grade which these proposals have is shown, in order to secure cycle stability, the electrode material is not improving greatly the situation of making the service capacity which it originally has losing in weight.

[0005]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the non-water rechargeable battery which aimed at coexistence of high service capacity and charge-and-discharge cycle stability, and was excellent in high capacity and cycle stability.

[0006]

[Means for Solving the Problem] This invention persons discovered that control for specific solvent composition of nonaqueous electrolyte especially existence of cyclic ether, a water content, and a free acid had a remarkable effect in solution of the above-mentioned technical problem, and resulted in this invention.

[0007] In the positive electrode which contains the material in which occlusion discharge is possible in reversible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery that consists of a separator, as for the technical problem of this invention, this nonaqueous electrolyte was solved for the water content more than 0.5 ppm including the cyclic ether below 7 volume % by the nonaqueous electrolyte rechargeable battery with which a part for 50 ppm or less and a free acid is characterized by 2 ppm or more being 100 ppm or less as HF an annular carbonate, a chain-like carbonate, and more than 0.1

[0008]

[Embodiments of the Invention] In this invention, although the following gestalten can be used, this invention is not limited to these.

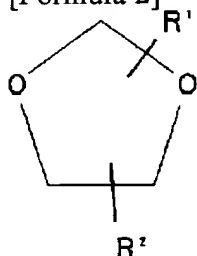
[0009] (1) The nonaqueous electrolyte rechargeable battery with which a water content is characterized [this nonaqueous electrolyte] by 2 ppm or more being 100 ppm or less by the amount of [50 ppm or less and] free acid as HF more than 0.5 ppm including the cyclic ether below 7 volume % in the positive electrode which contains the material in which occlusion discharge is possible in reversible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery that consists of a separator an annular carbonate, a chain-like carbonate, and more than 0.1 volume %.

[0010] (2) A nonaqueous electrolyte rechargeable battery given in the term 1 characterized by the lithium salt which this nonaqueous electrolyte contains containing LiPF₆ and LiBF₄.

[0011] (3) The term 1 to which this cyclic ether is characterized by what is expressed with the following general formula (1), or a nonaqueous electrolyte rechargeable battery given in 2.

[0012]

[Formula 2]



Even if respectively the same the inside R1 and R2 of a formula, it may differ, and it expresses a hydrogen atom or an eight or less-carbon number alkyl group.

[0013] (4) R1 of this cyclic ether, a nonaqueous electrolyte rechargeable battery given in the term 3 characterized by R2 being a hydrogen atom or a four or less-carbon number alkyl group.

[0014] (5) A nonaqueous electrolyte rechargeable battery given in any 1 term of the terms 1-4 to which the content of the annular carbonate in this electrolytic solution is characterized by the content of a chain-like carbonate being below 90 volume % more than 60 volume % below 30 volume % more than 5 volume %.

[0015] (6) A nonaqueous electrolyte rechargeable battery given in any 1 term of the terms 1-4 to which the content of a chain-like carbonate is characterized by the content of below 85 volume % and cyclic ether being below 5 volume % more than 0.3 volume % by the content of the annular carbonate in this electrolytic solution more than 71 volume % below 26 volume % more than 15 volume %.

[0016] (7) A nonaqueous electrolyte rechargeable battery given in any 1 term of the terms 1-6 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (2) at least.

[0017]

M1 M2 pM4 qM6 r General formula (2)

the inside of a formula, M1, and M2 -- difference -- Si, germanium, Sn, Pb, P, and B -- it is chosen out of aluminum and Sb -- at least -- a kind and M4 it is chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba -- at least -- a kind and M6 it is chosen out of O, S, and Te -- at least -- a kind, p, and q Each 0.001-10r The number of 1.00-50 is expressed.

[0018] Hereafter, the composition of the non-water rechargeable battery by 1 operation form of this invention is explained in detail.

[0019] As for the nonaqueous electrolyte used for the non-water rechargeable battery of this invention, a part for 50 ppm or less and a free acid is characterized by 2 ppm or more being 100 ppm or less by the water content as HF more than 0.5 ppm including the cyclic ether below 7 volume % an annular carbonate, a chain-like carbonate, and more than 0.1 volume %. The annular carbonate and chain-like carbonate and cyclic ether of an electrolytic-solution solvent are conventionally known, when using each independently, and when combining and using. Moreover, it is also known that reducing the moisture content and free-acid nature in the electrolytic solution generally will improve the charge-and-discharge

stability of a rechargeable battery. However, when a water content uses the negative-electrode material which has a cycle stabilization effect with remarkable the amount of [50 ppm or less and] free acid controlling to 2 ppm or more 100 ppm or less as HF, and is stated to especially the back more than 0.5 ppm including the cyclic ether below 7 volume % more than 0.1 volume %, it is new discovery that coexistence of high capacity and cycle stability can be aimed at.

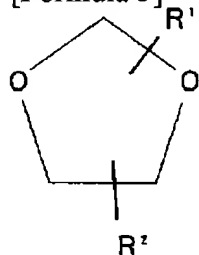
[0020] As an annular carbonate which can be used by this invention, ethylene carbonate, propylene carbonate, 1, 2-butylene carbonate, 2, 3-butylene carbonate, 1, 2-pentene carbonate, 2, and 3-pentene carbonate can be mentioned, for example. Especially ethylene carbonate is desirable in these.

[0021] As a chain-like carbonate, a carbon number can use the carbonate of the shape of a chain which is 3-8. In these, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methylethyl carbonate, methylpropyl carbonate, and ethyl propyl carbonate are desirable. Especially desirable things are dimethyl carbonate and diethyl carbonate. You may use dimethyl carbonate and diethyl carbonate together.

[0022] As cyclic ether which can be used in this invention, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, 1, 3-dioxane, 1, 4-dioxane, trioxanes, and these derivatives can be mentioned, for example. They are 1, 3-dioxolane, 1, 3-dioxane, 1, and 4-dioxanes and these derivatives, 1 expressed with the following general formula (1), 3-dioxolane, and its derivative more preferably.

[0023]

[Formula 3]



[0024] Even if respectively the same the inside R1 and R2 of a formula, it may differ, and it expresses a hydrogen atom or an eight or less-carbon number alkyl group. more -- desirable -- a hydrogen atom or a four or less-carbon number alkyl group -- they are a hydrogen atom, a methyl group, or an ethyl group especially preferably For example, the 1, 3-dioxolane, 2-methyl -1, 3-dioxolane, 2, and 2-dimethyl -1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, 2-ethyl -1, 3-dioxolane, 4-ethyl -1, 3-dioxolane, 2-methyl-4-ethyl -1, 3-dioxolane, etc. can be mentioned.

[0025] the mixing ratio of each solvent in the nonaqueous electrolyte of this invention -- the case of a rate where five to 30 volume % and a chain-like carbonate are [60 to 90 volume % and cyclic ether] 0.1 to 7 volume %s for an annular carbonate is desirable For an annular carbonate, ten to 28 volume % and a chain-like carbonate are [67 to 88 volume % and cyclic ether] the mixed ratios of 0.2 - 6 volume % more preferably. An annular carbonate is the case where 15 to 26 volume % and a chain-like carbonate are [71 to 85 volume % and cyclic ether] 0.3 to 5 volume %s, especially preferably.

[0026] Otherwise, the organic solvent of non-proton nature, such as gamma-butyrolactone, methyl formate, methyl-acetate, 1, 2-dimethoxyethane, dimethyl sulfoxide, formamide, dimethylformamide, acetonitrile, nitromethane, ethyl monochrome glyme, trialkyl phosphate, trimethoxy ethane, sulfolane, 3-methyl-2-oxazolidinone, ethyl ether, 1, and 3-propane ape ton, can be added to the nonaqueous electrolyte of this invention.

[0027] As a supporting electrolyte which can be used for the nonaqueous electrolyte of this invention, Li salts, such as LiClO₄, LiBF₄, LiPF₆, LiCF₃SO₃, LiCF₃CO₂, LiAsF₆ and LiSbF₆, LiB10Cl10, a low-grade aliphatic carboxylic-acid lithium, LiAlCl₄, LiCl, LiBr, LiI, a chloro borane lithium, and 4 phenyl lithium borate, can be mentioned, and these kinds or two sorts or more can be mixed and used, for example. Use of LiBF₄ or LiPF₆ is desirable especially. Furthermore, using combining LiBF₄ and LiPF₆ is desirable.

[0028] Although especially the concentration of a supporting electrolyte is not limited, its 0.2-3 mols per

11. of electrolytic solutions are desirable. Although especially the amount that adds these electrolytes in a cell is not limited, texture ***** can do it suitably with the amount of an electrode material, or the size of a cell.

[0029] The moisture content which the electrolyte of this invention contains has the fewest possible desirable one. 50 ppm or less have desirable moisture content, 40 ppm or less are more desirable, and especially 30 ppm or less are desirable. Although the minimum of a moisture content has a desirable method of a low, it is difficult to control below into 0.5 ppm. In order to lessen moisture content, while fully dehydrating beforehand the organic solvent and supporting electrolyte which are used when producing an electrolyte, it is required to maintain the atmosphere at the time of production at the state of low humidity. As for the atmosphere at the time of electrolyte production, it is good less than [minus 40 degree C] and to set a dew-point as less than [minus 50 degree C] more preferably. As for the produced electrolyte, saving under the atmosphere of the same low humidity is desirable. A moisture content can be measured with usual curl Fischer water measurement equipment.

[0030] A part for the free acid of this invention has desirable 100 ppm or less, its 80 ppm or less are more desirable, and especially its 60 ppm or less are desirable. Although the lower one of a minimum is desirable, it is difficult in cost to make it 2 ppm or less. In this invention, the amount of free acid is HF. The case where an unreacted part is carried in as a raw material of a supporting electrolyte, and a supporting electrolyte decompose under existence of moisture, and HF may be generated. Therefore, it is effective for refining of a supporting electrolyte and removal of moisture making the amount of free acid decrease. A part for a free acid can be decided by the method of using a bromine thymol blue as an indicator, carrying out a neutralization titration using 0.1 convention NaOH solution, and measuring etc.

[0031] Hereafter, the other materials and the manufacture method for making the nonaqueous electrolyte rechargeable battery of this invention are explained in full detail. positive and the negative electrode used for the nonaqueous electrolyte rechargeable battery of this invention -- a positive electrode -- a mixture or a negative electrode -- a mixture can be painted on a charge collector and can be made a positive electrode or a negative electrode -- everything but a positive active material or negative-electrode material can be looked like [a mixture], respectively, and can contain an electric conduction agent, a binder, a dispersant, a filler, an ion electric conduction agent, a pressure reinforcement agent, and various additives in it, respectively

[0032] As for the negative-electrode material used by this invention, it is desirable that it is mainly amorphous at the time of cell inclusion. It is the object which has the broadcloth dispersion band which mainly has the peak from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method [be / amorphous] using CuK alpha rays said here, and you may have a crystalline diffraction line. Among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value by the X diffraction using CuK alpha rays, the strongest intensity they are 500 or less times of the diffraction line intensity of the peak of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value -- desirable -- further -- desirable -- 100 or less times -- it is -- especially -- desirable -- 5 or less times -- it is -- most -- desirable -- It is not having a crystalline diffraction line.

[0033] As for the negative-electrode material used by this invention, being expressed with the following general formula (2) is desirable.

M1 M2 pM4 qM6 r General formula (2)

The inside of a formula, M1, and M2 It is it a kind that it is few as being chosen out of Si, germanium, Sn, Pb, P, B, aluminum, and Sb in difference, and is Si, germanium, Sn, P, B, and aluminum preferably, and they are Si, Sn, P, B, and aluminum especially preferably. M4 It is it a kind that it is few as being chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba, and is K, Cs, Mg, and calcium preferably, and they are Cs and Mg especially preferably. M6 It is it a kind that it is few as being chosen out of O, S, and Te, is O and S preferably, and is O especially preferably. p q It is 0.001-10 respectively, is 0.01-5 preferably, and is 0.01-2 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably. M1 and M2 Even if especially a valence is not limited and is an independent

valence, it may be the mixture of each valence. Moreover, M1, M2, and M4 A ratio is M2. And M4 M1 It can receive, can be made to change continuously in the range of the 0.001-10-mol equivalent, responds to it, and is M6. An amount (it sets to a general formula (2) and is the value of r) also changes continuously.

[0034] Also in the compound mentioned above, it sets to this invention, and is M1. The case where it is Sn is desirable and is expressed with a general formula (3).

[0035]

SnM3 pM5 qM7 r General formula (3)

The inside of a formula, and M3 It is it a kind that it is few as being chosen out of Si, germanium, Pb, and P, B and aluminum, and is Si, germanium, and P, B and aluminum preferably, and they are Si, and P, B and aluminum especially preferably. M5 It is it a kind that it is few as being chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba, is Cs and Mg preferably, and is Mg especially preferably. M7 It is it a kind that it is few as being chosen out of O and S, and is O preferably. p q It is 0.001-10 respectively, is 0.01-5 preferably, is 0.01-1.5 still more preferably, and is 0.7-1.5 especially preferably. r It is ** 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably.

[0036] Although the example of the negative-electrode material of this invention is shown below, this invention is not limited to these. SnAl 0.4B0.5P0.5K0.1O3.65 and SnAl0.4 B0.5 P0.5 Na 0.2O3.7, SnAl0.4 B0.3 P0.5 Rb 0.2O3.4, SnAl0.4 B0.5 P0.5 Cs0.4 O3.65, SnAl0.4 B0.5 P0.5 K0.1 germanium 0.05O3.85, SnAl0.4 B0.5 P0.5 K0.1 Mg0.1 germanium 0.02O3.83, and SnAl 0.4B0.4P0.4O3.2, SnAl 0.3B0.5P0.2O2.7 and SnAl 0.3B0.5P0.2O2.7, SnAl0.4 B0.5 P0.3 Ba0.08Mg 0.08O3.26, SnAl0.4 B0.4 P0.4 Ba 0.08O3.28, and SnAl 0.4B0.5P0.5O3.6, SnAl0.4 B0.5 P0.5 Mg 0.1O3.7, [0037] SnAl0.5 B0.4 P0.5 Mg0.1 F0.2 O3.65 and SnB0.5 P0.5 Li0.1 Mg 0.1F0.2O3.05, SnB0.5 P0.5 K0.1 Mg 0.1F0.2O3.05, SnB0.5 P0.5 K0.05Mg0.05F0.1 O3.03, and SnB0.5 P0.5 K0.05Mg 0.1F0.2O3.03, SnAl0.4 B0.5 P0.5 Cs0.1 Mg 0.1F0.2O3.65, SnB0.5 P0.5 Cs0.05Mg0.05F0.1 O3.03, and SnB0.5 P0.5 Mg 0.1F0.1O3.05 and SnB0.5 P0.5 Mg 0.1F0.2O3, SnB0.5 P0.5 Mg 0.1F0.06O3.07, SnB0.5 P0.5 Mg 0.1F0.14O3.03, SnPBa 0.08O3.58, SnPK 0.1O3.55, SnPK0.05Mg0.05O3.58, and SnPCs0.1 O3.55, [0038] SnPBa0.08F0.08O3.54 and SnPK0.1 Mg 0.1F0.2O3.55, SnPK0.05Mg0.05F0.1 O3.53, SnPCs0.1 Mg 0.1F0.2O3.55, SnPCs0.05Mg0.05F0.1 O3.53, and Sn1.1 aluminum0.4 B0.2 P0.6 Ba0.08F0.08O3.54, Sn1.1 aluminum0.4 B0.2 P0.6 Li0.1 K0.1 Ba 0.1F0.1O3.65, Sn1.1 aluminum0.4 B0.4 P0.4 Ba0.08O3.34, and Sn1.1 aluminum0.4 PCs 0.05O4.23, Sn1.1 aluminum0.4 PK 0.05O4.23, and Sn1.4 aluminum0.5 B0.3 P0.4 Cs 0.2O3.5, Sn1.2 aluminum 0.4B0.2P0.6 Ba 0.08O3.68 and Sn1.2 aluminum0.4 B0.2 P0.6Ba0.08F0.08O3.64, Sn1.2 aluminum0.4 B0.2 P0.6 Mg0.04Ba 0.04O3.68, Sn1.2 aluminum0.4 B0.3 P0.5 Ba 0.08O3.58, [0039] Sn1.3 aluminum0.3 B0.3 P0.4 Na 0.2O3.3, Sn1.3 aluminum0.2 B0.4 P0.4 calcium 0.2O3.4, Sn1.3 aluminum0.4 B0.4 P0.4 Ba 0.2O3.6, Sn1.4 aluminum0.4 PK 0.2O4.6, Sn1.4 aluminum0.2 Ba0.1 PK 0.2O4.45, and Sn1.4 aluminum0.2 Ba0.2 PK 0.2O4.6, Sn1.4 aluminum0.4 Ba0.2 PK0.2 Ba 0.1F0.2O4.9, Sn1.4 aluminum0.4 PK 0.3O4.65 and Sn1.5 aluminum0.2 PK 0.2O4.4, Sn1.5 aluminum0.4 PK 0.1O4.65, Sn1.5 aluminum0.4 PCs 0.05O4.63, Sn1.5 aluminum0.4 PCs0.05Mg 0.1F0.2O4.63, and SnSi0.5 aluminum0.1 B0.2 P0.1 calcium 0.4O3.1, SnSi0.4 aluminum 0.2B0.4O2.7 and SnSi0.5 aluminum0.2 B0.1 P0.1 Mg 0.1O2.8, [0040] SnSi0.6 aluminum 0.2B0.2O2.8, SnSi0.5 aluminum 0.3B0.4P0.2 O3.55 and SnSi0.5 aluminum0.3 B0.4 P0.5 O4.30 and SnSi0.6 aluminum 0.1B0.1P0.3O3.25 and SnSi0.6 aluminum0.1 B0.1 P0.1 Ba 0.2O2.95, SnSi0.6 aluminum0.1 B0.1 P0.1 calcium0.2 O2.95, and SnSi0.6 aluminum0.4 B0.2 Mg 0.1O3.2, SnSi0.6 aluminum 0.1B0.3P0.1O3.05, and SnSi0.6 aluminum0.2 Mg 0.2O2.7, SnSi0.6 aluminum0.2 calcium 0.2O2.7 and SnSi0.6 aluminum 0.2P0.2O3, SnSi 0.6B0.2P0.2O3, SnSi0.8 aluminum 0.2O2.9, SnSi0.8 aluminum 0.3B0.2P0.2O3.85, SnSi 0.8B0.2O2.9, [0041] SnSi0.8 Ba 0.2O2.8 and SnSi0.8 Mg 0.2O2.8, SnSi0.8 calcium 0.2O2.8 and SnSi 0.8P0.2O3.1, Sn0.9 Mn 0.3B0.4P0.4 calcium0.1 Rb0.1 O2.95 and Sn0.9 Fe0.3 B0.4 P0.4 calcium0.1 Rb 0.1O2.95 and Sn0.8 Pb0.2 calcium0.1 P0.9 O3.35 and Sn0.3 germanium0.7 Ba0.1 P0.9 O3.35 and Sn0.9 Mn0.1 Mg 0.1P0.9O3.35, Sn0.2 Mn0.8 Mg 0.1P0.9O3.35, Sn0.7 Pb0.3 calcium 0.1P0.9O3.35, Sn0.2 germanium0.8 Ba0.1 P0.9 O3.35[0042] Negative-electrode material is calcinated, for example and is obtained. The chemical formula of the compound which baking was carried out [above-mentioned] and obtained is computable from the weight difference of

the fine particles before and behind baking as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a shortcut method as a measuring method.

[0043] Although it is good until it approximates it to the deposition potential of the light metal, although 50-700-mol% per negative-electrode material of the amount of light metal insertion to the negative-electrode material of this invention is desirable, it is especially desirable, for example, [100-600 mol% of] Many the burst sizes are so desirable that there are to the amount of insertion. The insertion method of a light metal has electrochemical and the desirable chemical and thermal method. The method of inserting electrochemically the light metal contained in a positive active material and the method of electrochemical process of inserting directly electrochemically from a light metal or its alloy are desirable. The chemical method has mixture with a light metal, contact or an organic metal, for example, a butyl lithium etc., and the method of making it react. Electrochemical process and the chemical method are desirable. Especially this light metal has a lithium or a desirable lithium ion.

[0044] In this invention, by using the compound shown by the general formula (2) as shown above, and (3) mainly as a negative-electrode material, and the charge-and-discharge cycle property was more excellent, safety is high at high discharge voltage and high capacity, and the nonaqueous electrolyte rechargeable battery excellent in the current characteristic can be obtained. the especially excellent effect is acquired in this invention -- things are made -- a thing is using the compound with which Sn's is contained and the valence of Sn exists with divalent as a negative-electrode material It can ask for the valence of Sn by chemical titration operation. For example, it can analyze by the method of a publication to 165 pages of Physics and Chemistry of Glasses Vol.8 No.4 (1967). Moreover, it is also possible to determine from the Knight shift by solid-state nuclear-magnetic-resonance (NMR) measurement of Sn. For example, it sets to broad measurement and Metal Sn (Sn of 0 **) is Sn (CH₃)₄. To receiving and a peak appearing in a low magnetic field extremely with near 7000 ppm, in SnO (= divalent), it appears near 100 ppm, and appears near -600 ppm in SnO₂ (= tetravalence). Thus, since a Knight shift is greatly dependent on the valence of Sn which is a central metal when it has the same ligand, the determination of a valence is attained in the peak position required in 119 Sn-NMR measurement.

[0045] Various compounds can be included in the negative-electrode material of this invention. For example, transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, a lanthanoids system metal, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) and a periodic-table 17 group element (F, Cl) can be included. Moreover, the dopant of the various compounds (for example, compound of Sb, In, and Nb) which raise electronic-conduction nature may also be included. 0-20-mol% of the amount of the compound to add is desirable.

[0046] the synthesis method of the multiple oxide which makes a subject the oxide shown by the general formula (2) in this invention, and (3) -- the calcinating method and a solution method -- any method is employable

[0047] For example, it is M1 when the calcinating method is explained in detail. A compound and M2 A compound and M4 What is necessary is to mix a compound (for Si, germanium, Sn, Pb, P, B, aluminum, Sb, and M4 to be Mg, calcium, Sr, and Ba in difference for M1 and M2), and just to make it calcinate. As an Sn compound, for example, SnO, SnO₂, and Sn 2O₃, Sn₇ O₁₃ and [Sn 3O₄ and] H₂ O, Sn 8O₁₅, the first tin of hydroxylation, The second tin of oxy-hydroxylation, a stannous acid, a tin, the first tin of phosphoric acid, an ortho stannic acid, a metastannic acid, the Para stannic acid, a tin, the second tin of fluoridation, stannous chloride, a stannic chloride, the first tin of a pyrophosphoric acid, Lynn-ized tin, the first tin of sulfuration, a tin bisulfide, etc. can be mentioned.

[0048] As an Si compound, hydro silane compounds, such as alkoxysilane compounds, such as organosilicon compounds, such as SiO₂, SiO, a tetramethylsilane, and a tetraethyl silane, a tetramethoxy silane, and a tetrapod ethoxy silane, and a TORIKURORO hydro silane, can be mentioned.

[0049] As a germanium compound, alkoxy germanium compounds, such as GeO₂, GeO, a germanium tetrapod methoxide, and germanium tetrapod ethoxide, etc. can be mentioned.

[0050] As a Pb compound, PbO₂, PbO, Pb 2O₃, Pb 3O₄, a lead nitrate, a lead carbonate, a lead formate, lead acetate, a lead tetraacetate, tartaric-acid lead, lead JIETOKISHIDO, lead diisopropoxide, etc. can be

mentioned.

[0051] As a P compound, a phosphorus pentaoxide, phosphorus oxychloride, a phosphorus pentachloride, a phosphorus trichloride, phosphorus tribromide, a trimethyl phosphoric acid, a triethyl phosphoric acid, a TORIPURO pill phosphoric acid, the first tin of a pyrophosphoric acid, phosphoric-acid boron, etc. can be mentioned.

[0052] As a B compound, for example, 32 boron oxide, boron trichloride, boron tribromide, a boron carbide, a way acid, way acid TORIMECHIRU, way acid triethyl, tripropyl borate, way acid tributyl, Lynn-ized boron, phosphoric-acid boron, etc. can be mentioned.

[0053] As an aluminum compound, an aluminum oxide (an alpha alumina, beta alumina), an aluminum silicate, aluminum tree iso-propoxide, tellurous-acid aluminum, an aluminum chloride, HOU-ized aluminum, Lynn-ized aluminum, an aluminium phosphate, lactic-acid aluminum, way acid aluminum, an aluminum sulfate, an aluminum sulfate, HOU-ized aluminum, etc. can be mentioned.

[0054] As a Sb compound, for example, 3 oxidization 2 antimony; triphenyl antimony, etc. can be mentioned.

[0055] As Mg, calcium, Sr, and a Ba compound, each oxidization salt, a hydroxylation salt, a carbonate, phosphate, a sulfate, a nitrate, an aluminium compound, etc. can be mentioned.

[0056] As baking conditions, it is 6 degrees C or more 2000 degrees C or less that it is 2000 degrees C or less of 4-degree-C [or more]/m programming rates as a programming rate desirable still more preferably. Are 10 degrees C or more 2000 degrees C or less, and it is especially preferably desirable as a burning temperature that it is [250 degrees-C or more] 1500 degrees C or less. It is 350 degrees C or more 1500 degrees C or less still more preferably, and is 500 degrees C or more 1500 degrees C or less especially preferably. And it is desirable that it is 100 or less hours as a firing time for 0.01 hours or more. It is 70 or less hours still more preferably for 0.5 hours or more, and is 20 or less hours especially preferably for 1 hour or more. And it is below 4-degree-Cor more 107 ** that it is below 2-degree-C[or more]/m 107 ** as a temperature fall speed desirable still more preferably, and it is below 6-degree-Cor more 107 ** especially preferably, and is below 10-degree-Cor more 107 ** especially preferably.

[0057] The programming rate in this invention is the mean velocity of a temperature rise until it reaches "80% of burning temperature (degree-C display)" from "50% of burning temperature (degree-C display)", and the temperature fall speed in this invention is the mean velocity of a temperature reduction until it reaches "50% of burning temperature (degree-C display)" from "80% of burning temperature (degree-C display)."

[0058] You may cool in a firing furnace and a temperature fall is taken out out of a firing furnace again, for example, may be supplied underwater and may be cooled. moreover, the gun method, the Hammer-Anvil method, and the slap method given in 217 pages (Gihodo Shuppan Co., Ltd. 1987) of ceramic processing -- the - gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and melt Super-quenching methods, such as the drag method, can also be used. Moreover, you may cool using the single roller method given in 172 pages (Maruzen 1991) of new glass handbooks, and a congruence roller. In the case of the material fused during baking, you may take out a baking object continuously, supplying a raw material during baking. It is desirable to stir a melt in the case of the material fused during baking.

[0059] Oxygen content is the atmosphere below 5 volume % preferably, and baking gas atmosphere is inert gas atmosphere still more preferably. Nitrogen, an argon, helium, a krypton, a xenon, etc. are mentioned as inert gas.

[0060] The average grain size of the compound shown by the general formula (2) used by this invention and (3) is 0.1-60 micrometers. It is desirable and is 1.0-30 micrometers. It is especially desirable and is 2.0-20 micrometers. It is still more desirable. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. At the time of pulverization, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification in order to consider as a desired particle size. As the classification method, there is especially no limitation

and it can use a screen, a pneumatic elutriation machine, an elutriation, etc. if needed. A classification can use dry type and wet.

[0061] It is more desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) may be set to 0.3-2.2 as a desirable lithium content transition-metals oxide positive-electrode material rather than being used by this invention. As an especially desirable lithium content transition-metals oxide positive-electrode material with which it is used by this invention, it is desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) may be set to 0.3-2.2.

[0062] It is desirable that an especially desirable lithium content transition-metals oxide positive-electrode material used by this invention is Li_xQO_y (Q is mainly the transition metals in which a kind contains Co, Mn, nickel, V, and Fe at least, $x=0.2-1.2$, and $y=1.4-3$ here). As Q, you may mix aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. in addition to transition metals. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0063] As a still more desirable lithium content metallic-oxide positive-electrode material used by this invention Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , and $\text{Li}_x\text{Coa nickel1-a O}_2$, $\text{Li}_x\text{Cob V1-b Oz}$ and $\text{Li}_x\text{Cob Fe1-b O}_2$, $\text{Li}_x\text{Mn 2O}_4$, $\text{Li}_x\text{Mnc Co2-c O}_4$, and $\text{Li}_x\text{Mnc nickel2-c O}_4$, $\text{Li}_x\text{Mnc V2-c O}_4$ and $\text{Li}_x\text{Mnc Fe2-c O}_4$ (it is $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-2.3$ here) are raised.

[0064] As most desirable lithium content transition-metals oxide positive-electrode material used by this invention, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{Coa nickel1-aO}_2$, $\text{Li}_x\text{Mn 2O}_4$, and $\text{Li}_x\text{Cob V1-b Oz}$ (it is $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.9$ to 0.98 , and $z=2.01-2.3$ here) are raised. Here, the x above-mentioned values are values before a charge-and-discharge start, and are fluctuated by charge and discharge.

[0065] If it is the electronic-conduction nature material which does not cause a chemical change in the constituted cell as a conductive carbon compound which can be used by this invention, it is good anything. As an example, carbon black, such as graphite, such as artificial graphites, such as elevated-temperature baking objects, such as natural graphites, such as a flaky graphite, a scale-like graphite, and an earthy graphite, petroleum coke, coal corks, celluloses, a saccharide, and a mesophase pitch, and a vapor-growth graphite, acetylene black, furnace black, KETCHIEN black, channel black, lamp black, and thermal black, an asphalt pitch, a coal tar, activated carbon, a meso fuze pitch, the poly acene, etc. can be raised. In these, graphite and carbon black are desirable.

[0066] As electric conduction agents other than a carbon system, independent or such mixture can be included for conductive metallic oxides, such as conductive whiskers, such as metal powders, such as conductive fiber, such as a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and a potassium titanate, and titanium oxide, etc. if needed.

[0067] As for the addition to the binder layer of an electric conduction agent, it is desirable that it is 6 - 50 % of the weight to negative-electrode material or positive-electrode material, and it is especially desirable that it is 6 - 30 % of the weight. in carbon or a graphite, it is 6 - 20 % of the weight -- especially, it is desirable

[0068] the electrode used by this invention -- as a binder for holding a mixture, kinds of the polymer which has polysaccharide, thermoplastics, and rubber elasticity, or such mixture can be used As a desirable binder, starch, a carboxymethyl cellulose, A cellulose, a diacetyl cellulose, a methyl cellulose, a hydroxyethyl cellulose, Hydroxypropylcellulose, alginic-acid Na, a polyacrylic acid, Polyacrylic-acid Na, a polyvinyl phenol, a polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, a polyacrylamide, Water-soluble polymer, such as PORIHIDOROKISHI (meta) acrylate and a styrene-maleic-acid copolymer, Polyvinyl chloride, poly tetrapod FURURO ethylene, a polyvinylidene fluoride, A tetrapod FURORO ethylene-hexa FURORO propylene copolymer, a vinylidene fluoride-tetrapod FURORO ethylene-hexa FURORO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, a polyvinyl-acetal resin, a methylmetaacrylate, The acrylic-ester (meta) copolymer containing acrylic esters (meta), such as 2-

ethylhexyl acrylate The polyvinyl ester copolymer containing vinyl esters, such as an acrylic-ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, A polybutadiene, neoprene rubber, a fluororubber, a polyethylene oxide, An emulsion (latex) or suspensions, such as a polyester polyurethane resin, a polyether polyurethane resin, a polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. The latex of a polyacrylic ester system, a carboxymethyl cellulose, a polytetrafluoroethylene, and a polyvinylidene fluoride are especially desirable.

[0069] these binders are independent -- or it can mix and use if there are few additions of the binder -- an electrode -- if the holding power and cohesive force of a mixture are weak, and cycle nature is bad and there is again, electrode volume will increase, an electrode unit volume or the capacity per unit weight will decrease, conductivity falls further and capacity decreases [too many] Although especially the addition of a binder is not limited, its 1 - 30 % of the weight is especially desirable, and its 2 - 10 % of the weight is desirable.

[0070] the negative electrode of this invention -- a mixture or a positive electrode -- a mixture -- it is desirable to perform adjustment of a paste by the drainage system

[0071] a mixture -- an active material and an electric conduction agent are mixed first, a binder (the suspension of resin fine particles or emulsion (latex)-like thing) and water are added, kneading mixture is carried out, succeedingly, it can distribute by stirring mixers, such as a mixer, a homogenizer, a dissolver, a planetary mixer, a paint shaker, and a sand mill, and the disperser, and adjustment of a paste can be performed

[0072] the adjusted mixture of a positive active material or a negative-electrode active material -- on a charge collector, a paste is applied, (coat) dried and compressed and is mainly used Although an application can be performed by various methods, the reverse rolling method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the dipping method, and the squeeze method can be mentioned, for example. The blade method, the knife method, and the extrusion method are desirable. As for an application, it is desirable to carry out the speed for 0.1-100m/. under the present circumstances, a mixture -- according to the liquid nature of a paste, and a drying property, the surface state of a good application layer can be obtained by selecting the above-mentioned method of application Although the thickness, length, and width of the application layer are decided with the size of a cell, the thickness of an application layer is in the state compressed after dryness, and especially its 1-2000 micrometers are desirable.

[0073] the method generally adopted can be used as a pellet, or the dryness for moisture removal of a sheet or the dehydration method, and independent in hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and a damp wind -- or it can combine and use The range of temperature of 80-350 degrees C is desirable, and its range which is 100-250 degrees C is especially desirable. moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively in respect of charge-and-discharge cycle nature

[0074] a sheet-like electrode -- although compression of a mixture can use the press method generally adopted, a die-press method and its calender pressing method are especially desirable Especially press ** is 10 kg/cm² - 3 t/cm², although not limited. It is desirable. The press speed of the calender pressing method has the amount of desirable 0.1-50m/. Press temperature has desirable room temperature -200 degree C.

[0075] As the quality of the material, in a positive electrode, it is aluminum, stainless steel, nickel, titanium, or these alloys, the base materials, i.e., the charge collector, of the positive electrode which can be used by this invention, and a negative electrode, they are copper, stainless steel, nickel, titanium, or these alloys at a negative electrode, and are a foil, an expanded metal, a punching metal, and a wire gauze as a gestalt. Especially, in a positive electrode, copper foil is desirable to an aluminum foil and a negative electrode.

[0076] The separator which can be used by this invention has large ion transmittance, and it has a predetermined mechanical strength, and that what is necessary is just an insulating thin film, as the

quality of the material, olefin system polymer, fluorine system polymer, cellulose system polymer, a polyimide, nylon, a glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporosity film are used as a gestalt. Especially, as the quality of the material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are desirable, and what is a microporosity film as a gestalt is desirable. Especially, the microporosity film whose thickness and aperture is 0.01-1 micrometer and is 5-50 micrometers is desirable.

[0077] Drawing 1 is the cross section showing an example of a cylinder type cell. The configuration of a cell is applicable to both a button, coin, a sheet, a cylinder, an angle, etc. A cell inserts in the cell can 2 the electrode sheets 4 and 5 wound with a pellet, the shape of a sheet, and the separator 3, connects an electrode with a can electrically, and the electrolytic solution 6 is poured in, and it obturates and forms it. The internal free-wheel-plate object 10 equipped with the ring 11 fits into the up mouth of the cell can 2 through the gasket 1 made from polypropylene, and the positive-electrode cap 8 who serves as a positive-electrode terminal is exposed in the upper part. At this time, a relief valve 7 (explosion-proof valve element) can be used as an obturation board. Furthermore, in order to guarantee the safety of a cell, it is desirable to use the PTC element 9.

[0078] The closed-end cell sheathing cans which can be used by this invention are the steel board which performed nickel plating as the quality of the material, a stainless steel plate (SUS304, SUS304 L, SUS304 N, SUS316, SUS316 L, SUS430, SUS444 grade), the stainless steel plate (same as the above) which performed nickel plating, aluminum or its alloy, nickel, titanium, and copper, and are perfect circle form tubed one, ellipse form tubed one, square tubed, and rectangle tubed as a configuration. Especially when a sheathing can serves as a negative-electrode terminal, a stainless steel plate and the steel board which performed nickel plating are desirable, and when a sheathing can serves as a positive-electrode terminal, a stainless steel plate, aluminum, or its alloy is desirable.

[0079] the mixture of the shape of this sheet -- an electrode is rolled or folded, is inserted in a can, connects a sheet with a can electrically, pours in an electrolyte, and forms a cell can using an obturation board. At this time, a relief valve can be used as an obturation board. It may be equipped with the various safe elements known from the former besides a relief valve. For example, a fuse, bimetal, a PTC (right temperature coefficient) element, etc. are used as an overcurrent-protection element. Moreover, the method, the gasket crack method, or the obturation board crack method of making a cut in a cell can can be used for everything but a relief valve as a cure of internal pressure elevation of a cell can. Moreover, you may make the circuit which built the surcharge and the cure against an overdischarge into the charge machine provide.

[0080] Although an electrolyte may pour in the whole quantity at once, it is desirable to carry out by dividing into two or more stages. When dividing and pouring into two or more stages, the composition (after pouring in the solution which dissolved lithium salt in the non-aqueous solvent or the non-aqueous solvent, the solution which dissolved lithium salt in a non-aqueous solvent or a non-aqueous solvent with viscosity higher than the aforementioned solvent is poured in) which is different also by the same composition is sufficient as each liquid. Moreover, a cell can may be decompressed for shortening of electrolytic pouring time etc. (preferably 500 - 1 torr, more preferably 400 - 10 torr), or you may perform applying a centrifugal force and an ultrasonic wave to a cell can.

[0081] A metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A well-known method (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0082] As the quality of the material, they are olefin system polymer, fluorine system polymer, cellulose system polymer, a polyimide, and a polyamide, from organic-solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has desirable olefin system polymer, and especially its polymer of a propylene subject is desirable. Furthermore, it is desirable that it is the

block copolymerization polymer of a propylene and ethylene.

[0083] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, an adhesive tape, a metal film, paper, cloth, a paint, a plastics case, etc. Moreover, the portion of sheathing discolored with heat in part at least is prepared, and you may make it the heat history in use known.

[0084] The cell of this invention constructs two or more in series and/or in parallel if needed, and is contained by the cell pack. You may prepare a safety circuit (circuit with the function which intercepts current if it acts as the monitor of the voltage of each cell and/or the whole group cell, temperature, the current, etc. and is required) besides safe elements, such as a right temperature coefficient resistor, a thermal fuse, a fuse, and/or a current interception element, in a cell pack. Moreover, the positive electrode of each cell and a negative-electrode terminal, the whole group cell and the temperature element child of each cell, the current element child of the whole group cell, etc. can also be prepared in a cell pack as an external terminal in addition to the positive electrode of the whole group cell, and a negative-electrode terminal. Moreover, you may build voltage conversion circuits (DC-DC converter etc.) in a cell pack. Moreover, it may fix by welding a lead board, and you may fix connection of each cell so that it can detach and attach easily with a socket etc. Furthermore, you may prepare display functions, such as cell remaining capacity, existence of charge, and a usage count, in a cell pack.

[0085] The cell of this invention is used for various devices. It is desirable to be especially used for a video movie, a carrying type videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, a compact camera, a single-lens reflex camera, a disposable camera, a notebook sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, an automobile, etc.

[0086]

[Example] Although an example is given to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0087] [positive electrode -- a mixture -- creation] of a paste -- LiCoO_2 of a positive active material It made as follows. What mixed a lithium carbonate and 4 oxidization 3 cobalt by the mole ratio of 3:2 is put into an alumina crucible, among air and after carrying out a temperature up to 750 degrees C and carrying out temporary quenching to them at 2 degrees C/m for 4 hours, it calcinates at 900 degrees C at the speed of 2 degrees C/m further for 8 hours at the temperature of temperature up *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne., and it grinds after that, and is LiCoO_2 . Particle powder was created. Created LiCoO_2 The 0.6 mS/m specific surface area [electric conductivity / of dispersion liquid when, as for a particle, centriole child size distributes 5 micrometers and 50g of washing articles in 100ml water] / according / pH / to 10.1 and a nitrogen adsorption process was 0.42m² / g. this LiCoO_2 200g of particles, and acetylene black 10g -- a homogenizer -- mixing -- continuing -- as a binder -- 2-ethylhexyl acrylate, an acrylic acid, 8g (50 % of the weight of solid-content concentration) of water distribution objects of the copolymer of acrylonitrile, and carboxymethyl-cellulose solution of 2 % of the weight of concentration -- 60g -- adding -- kneading mixture -- carrying out -- further -- 50g of water -- adding -- a homogenizer -- stirring mixture -- carrying out -- a positive electrode -- a mixture -- the paste was created

[0088] [negative electrode -- a mixture -- creation] of a paste -- $\text{SnGe}_{0.1}\text{B}_{0.5}\text{P}_{0.58}\text{Mg}_{0.1}\text{K}_{0.1}\text{O}_{3.35}$ (6.7g of tin protoxides) 10.3g of pyrophosphoric-acid tin, 1.7g of boron oxides, 0.7g of potassium carbonate, 0.4g [of magnesium oxides] and diacid-ized germanium 1.0g is blended dryly. Put into the crucible made from an alumina and a temperature up is carried out to 1100 degrees C by part for bottom 15-degree-C/of argon atmosphere. After calcinating at 1100 degrees C for 12 hours, what lowered even to the room temperature by part for 10-degree-C/, and was taken out from the firing furnace is collected. What was ground with the jet mill (it is the object which has the broadcloth peak which has the peak near 28 degree with 2theta value in the X-ray diffraction method using 4.5 micrometers of mean particle diameters, and CuK alpha rays, and the crystalline diffraction line was not looked at by 40 degrees or more 70 degrees or less with 2theta value.) 30g is mixed with a homogenizer. 200g and an electric conduction agent (artificial graphite) -- what furthermore added 50g of carboxymethyl-cellulose solution

of 2 % of the weight of concentration, and 10g of polyvinylidene fluorides as a binder, and was mixed -- further -- water -- 30g -- adding -- kneading mixture -- carrying out -- a negative electrode -- a mixture -- paste F-1 was created The polyvinylidene fluoride used about 0.1-micrometer particle.

[0089] a negative electrode -- a mixture -- 30g of pastes F-2 was added, kneading mixture was carried out further and they made 230g of the thing and water which added 50g of carboxymethyl-cellulose solution of 2 % of the weight of concentration, and 10g of polyvinylidene fluorides using commercial petroleum coke (the product made from Japanese PETOROREMU, PC-R), and were mixed

[0090] [creation of a positive electrode and a negative-electrode electrode sheet] -- the positive electrode created above -- a mixture -- after having applied the paste to both sides of an aluminum foil charge collector with a thickness of 30 micrometers by the blade coating machine so that the thickness of the sheet after coverage 400 g/m² and compression might be set to 280 micrometers, and drying it, compression molding was carried out with the roller-press machine, it judged in the predetermined size, and the band-like positive-electrode sheet was created Furthermore, dehydration dryness was enough carried out at the far-infrared heater in the dry box (dew-point; dry air -50 degrees C or less), and the positive-electrode sheet was created.

[0091] the same -- a negative electrode -- a mixture -- paste F-1 and F-2 were applied to the 20-micrometer copper foil charge collector, and the negative-electrode sheets A and B whose thickness of the sheet after compression is 90 micrometers were created, respectively by the same method as the above-mentioned positive-electrode sheet creation

[0092] [Electrolyte adjustment] In argon atmosphere, 80ml diethyl carbonate (DEC) was put into the polypropylene container of a 200 cc thin mouth, and the 20ml ethylene carbonate (EC) was dissolved small quantity every, taking care that solution temperature does not exceed 30 degrees C to this. Next, to this mixed solvent, they are 0.469g LiBF₄ and 14.43g LiPF₆ as a supporting electrolyte. It dissolved in the above-mentioned mixed solvent small quantity every in above order, taking care that solution temperature does not exceed 30 degrees C. The obtained electrolyte was a transparent and colorless liquid by specific gravity 1.135. The amount of [18 ppm (Kyoto electron make tradename MKC-210 type car RUF1 shear water measurement equipment measurement) and] free acid of moisture was 20 ppm (the bromthymol blue is used as an indicator, a neutralization titration is carried out using decinormal NaOH solution, and it measures). This electrolyte is set to C-1 for comparison.

[0093] Furthermore, the electrolyte A by this example as well as an electrolyte C-1 was made except mixing ether according to the following table 1 after DEC and EC. In addition, adjustment of an electrolyte was performed using the chemical and container which were fully dehydrated in the dry booth (dew-point minus 60 degree C dry air). In the following table 1, that from which what has a supporting electrolyte the same as an electrolyte C-1 differs in combined use, a publication, and composition was indicated under the table.

[0094]

[Table 1]

Electrolytic composition electrolyte The amount of DEC The amount of EC Addition solvent kind
Addition Supporting electrolyte Moisture content Number for a free acid ml ml ml ppm ppm C-1 80 20
Nothing 0 Combined use 8 20C-2 80 20 1, 3-dioxolane 0.01 Combined use 8 20A-1 80 20 Same as the
above 0.1 Combined use 8 20A-2 79.8 19.9 Same as the above 0.3 Combined use 8 20A-3 79.6 19.9 The
same as the above 0.5 Combined use 8 20A-4 78 19.5 Same as the above 2.5 Combined use 8 20A-5 77.6
19.4 The same as the above 3.0 Combined use 8 20A-6 76 19 Same as the above 5.0 Combined use 8
20A-7 74.5 18.5 The same as the above 7.0 Combined use 8 20A-8 95 5 Same as the above 0.1
Combined use 8 20A-9 70 30 Same as the above 0.1 Combined use 8 20A-10 78 19.5 Tetrahydrofuran
2.5 Combined use 8 20A-11 79.6 19.9 Tetrahydropyran 0.5 Combined use 8 20A-12 78 19.5 1, 3-
dioxane 2.5 Combined use 8 20A-13 78 19.5 1, 4-dioxane 2.5 Combined use 8 20A-14 78 19.5 1, 3-
dioxolane 2.5 Independent *1 8 20C-3 78 19.5 Same as the above 2.5 Combined use 60 120C-4 72 18
The same as the above 10 Combined use 8 20C-5 80 With no 20 0 Independent *1 8 20C-6 80 20 1, 3-
dioxolane 0.01 Independent *1 8 20 Independent *1 is LiPF₆. 15.19g was used.

[0095] [Creation of a cylinder cell] As shown in drawing 1, the laminating was carried out to the order

of positive-electrode sheet 5, separator made from microporosity polypropylene film, and negative-electrode sheet A (4), and a separator 3, and this was wound in the shape of a whorl. It contained with the iron closed-end cylindrical cell can 2 which performed nickel plating which serves this winding object as a negative-electrode terminal. Furthermore, the electrolyte given in Table 1 was poured in into the cell can 2 as an electrolyte 6. the cell lid 8 which has a positive-electrode terminal, the PTC element 9, and explosion-proof valve element 7 grade -- piling up -- a gasket 1 -- minding -- the cylindrical cell was created in total

[0096] About the cell created by the above-mentioned method, charge and discharge were carried out on condition that current density 5 mA/cm², charge final-voltage 4.1V, and discharge-final-voltage 2.8V, and service capacity and the cycle life were searched for.

[0097] The cycle nature (300th capacity to the 1st charge and discharge comparatively) of each cell is shown in Table 2. Service capacity is shown as a relative value when setting the cell numbers 1 and 21 to 100.

[0098]

[Table 2]

A cell number	A negative-electrode sheet	Electrolyte number	Service capacity	Cycle nature
Comparison cell A C-1	100	682	Same as the above A C-2	100
682	Same as the above A A-1	100	804	
804	Same as the above A A-2	100	825	
825	Same as the above A A-3	100	826	
826	Same as the above AA-4	99	867	
867	Same as the above A A-5	99	848	
848	Same as the above A A-6	99	829	
829	same as the above A A-7	98	7810	
7810	Same as the above A A-8	100	7411	
7411	Same as the above A A-9	99	7812	
7812	Same as the above A A-10	98		
	7313	Same as the above A A-11	98	7114
7114	Same as the above A A-12	98	7515	
7515	Same as the above A A-13	98	7216	
7216	Same as the above A A-14	99	8217	
8217	Comparison cell A C-3	91	5918	
5918	Same as the above A C-4	96	6919	
6919	Same as the above A C-5	100	6720	
6720	Same as the above A C-6	100	6721	
6721	Same as the above B C-1	100	6922	
6922	This example cell B A-4	99	8923	
8923	Same as the above B A-14	99	8624	
8624	Comparison cell B C-5	99	68	

[0099] The moisture content of an electrolyte C-3 is 60 ppm, and the amount of free acid of the comparison cell number 17 is 120 ppm. By this example, the cell using the electrolyte a moisture content is 8 ppm and the amount of [whose] free acid is 20 ppm was created to it. Service capacity and cycle nature had a large direction with few parts for an electrolytic moisture content and a free acid, and the good result was obtained. An electrolytic moisture content has desirable 50 ppm or less, and a part for a free acid has desirable 100 ppm or less. However, it is difficult to control a moisture content to 0.5 ppm or less, and it is difficult in cost to control a part for a free acid to 2 ppm or less. Therefore, as for an electrolyte, it is desirable that a moisture content is [the amount of 0.5 ppm or more 50 ppm or less and a free acid] 2 ppm or more 100 ppm or less.

[0100] As for the comparison cell numbers 1, 2, 19, 20, 21, and 24, cyclic ether is altogether contained in the electrolyte for below 0.01 volume %. 10 volume % As for the comparison cell number 18, cyclic ether is contained in the electrolyte. 0.1-7.0 volume % As for the cell numbers 3-16 by this example, and 22 and 23, cyclic ether is contained in the electrolyte to it. The cell by this example has greatly good cycle nature. As for an electrolyte, it is desirable that the cyclic ether below 7 volume % is included more than 0.1 volume %. In this case, it is desirable that five to 30 volume % and a chain-like carbonate are others [cyclic ether], and an annular carbonate is 60 to 90 volume %. For an annular carbonate, 15 to 26 volume % and a chain-like carbonate are [71 to 85 volume % and cyclic ether] the mixed ratios of 0.3 - 5 volume % especially preferably.

[0101] The cell number 16 of this example is LiPF₆ as a directions salt to an electrolyte A-14. It used.

The cell number 6 by this example is LiBF₄ as a supporting electrolyte to an electrolyte A-4 to it. LiPF₆

It used together. LiBF₄ LiPF₆ Cycle nature becomes large and has the good direction used together. An

electrolyte is LiBF₄ as a supporting electrolyte. LiPF₆ Containing is desirable.

[0102]

[Effect of the Invention] If the electrolytic solution which specified a part for a free acid as the moisture

content is used like this invention using the cyclic ether of an annular carbonate, a chain-like carbonate,

and the amount of specification, the non-water rechargeable battery with which service capacity and

cycle nature were compatible can be made. Especially this effect is large when a predetermined oxide is

used for a negative electrode.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

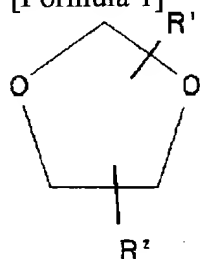
[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery with which a water content is characterized [this nonaqueous electrolyte] by 2 ppm or more being 100 ppm or less by the amount of [50 ppm or less and] free acid as HF more than 0.5 ppm including the cyclic ether below 7 volume % in the positive electrode which contains the material in which occlusion discharge is possible in reversible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery that consists of a separator an annular carbonate, a chain-like carbonate, and more than 0.1 volume %.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the lithium salt which this nonaqueous electrolyte contains containing LiPF₆ and LiBF₄.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 or 2 with which this cyclic ether is characterized by what is expressed with the following general formula (1).

[Formula 1]



Even if respectively the same the inside R1 and R2 of a formula, it may differ, and it expresses a hydrogen atom or an eight or less-carbon number alkyl group.

[Claim 4] R1 of this cyclic ether, the nonaqueous electrolyte rechargeable battery according to claim 3 characterized by R2 being a hydrogen atom or a four or less-carbon number alkyl group.

[Claim 5] A nonaqueous electrolyte rechargeable battery given in any 1 term of the claims 1-4 to which the content of the annular carbonate in this electrolytic solution is characterized by the content of a chain-like carbonate being below 90 volume % more than 60 volume % below 30 volume % more than 5 volume %.

[Claim 6] A nonaqueous electrolyte rechargeable battery given in any 1 term of the claims 1-4 to which the content of a chain-like carbonate is characterized by the content of below 85 volume % and cyclic ether being below 5 volume % more than 0.3 volume % by the content of the annular carbonate in this electrolytic solution more than 71 volume % below 26 volume % more than 15 volume %.

[Claim 7] A nonaqueous electrolyte rechargeable battery given in any 1 term of the claims 1-6 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (2) at least.

M1 M2 pM4 qM6 r General formula (2)

the inside of a formula, M1, and M2 -- difference -- Si, germanium, Sn, Pb, P, and B -- it is chosen out

of aluminum and Sb -- at least -- a kind and M4 it is chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba -- at least -- a kind and M6 it is chosen out of O, S, and Te -- at least -- a kind, p, and q Each 0.001-10r The number of 1.00-50 is expressed.

[Translation done.]